INITIAL QUALITY CONTROL RESULTS FROM A CANADIAN WATER QUALITY ASSESSMENT NETWORK

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ABSTRACT

The Western and Northern Region Water Quality Branch of Environment Canada contributes to the National Water Quality Assessment Program by routinely sampling a number of streams and lakes located throughout the prairie provinces and the Northwest Territories. In order to control the overall quality of the results contributed to the Program, the Branch instituted a Field Quality Control Project which consists of collecting a selected number of samples in triplicate. The Project was started in 1977. This report presents the results for nutrient parameters (Carbon, Nitrogen and Phosphorus). The total precision is estimated as the median of the coefficients of variation computed on sets of three observations. For eight of the 12 parameters for which analytical precisions are available, the total precision was less than or equal to the analytical precision. However, when maximum coefficients are combined with total precision in a simple classification scheme, only four parameters can be said to have "good" precision. Possible factors which might influence precision such as concentration, river discharge, and the time interval between sampling and receipt in the laboratory, showed no definite correlation. Examination of the 20 sets with the highest coefficients points to a wide variety of random factors which cause poor precision.

INTRODUCTION

Substantial effort has generally gone into assessing the accuracy and precision of lab procedures whereas little or no work has been done on establishing the accuracy and precision of field procedures. It is recognized that knowledge of the accuracies and precisions associated with the field and lab procedures is paramount for a scientifically sound interpretation of the data obtained from all programs (Water Quality Branch, 1978). It is incumbent on data collectors to be as accurate and precise as practically feasible since it is not always known, at the time of collection, to what end the data will serve. Separating and quantifying field and lab precision cannot be achieved without

considerable difficulty and cost. Therefore, the Water Quality Branch, Western and Northern Region, embarked on a program to establish total precision. The Field Quality Control Project of the Branch was started in June of 1977 with the objective of estimating the total precision of the data collected by the Branch for the full parametric spectrum. This report considers only the nutrient parameters.

There are two purposes to this report. First, estimates will be made of the total precision of the nutrient parameters; and, second, possible causes for poor precision in these parameters will be explored. Although the detection of causes was not an objective of the project, the results should point out any weak links that might exist in the sample handling and analysis process.

In order to clarify the discussion, a number of terms must be defined. These definitions must be considered semantically rigid for the purpose of this report. A "set" refers to two or three samples collected from the same location over a short period of time, usually less than one hour, and treated identically from collection to data reporting. A "group" refers to a number of sets which share some common attribute, such as having all been collected in the same fiscal year or from the same site. "Precision" is the degree of reproducibility of the measurement. It can be expressed mathematically as the coefficient of variation (CV), in %, of a set. The coefficient of variation, which is an indicator of relative dispersion, is used in this report in order to compare results from different rivers sampled at various times over a five-year period. It also allows us to compare the relative performance of different parameters. Correlation between precisions and other sampling factors refers solely to the degree of linear association between a statistic and an independent variable.

DATA

The data for this report were collected between June of 1977 and March of 1982. The sets were collected from 127 sites in the Western and Northern Region, which encompasses the prairie provinces and the Northwest Territories.

The basis of the project design was to collect in triplicate a number of routine samples collected as part of the on-going Water Quality Assessment Program. The first year of the Field Quality Control Project was designed to be an intensive first determination of measurement uncertainties. In that year, nearly every sample collected by Branch staff was triplicated. Beginning in April of 1978, all sites of the Water Quality Assessment Program were included in the project on a rotating basis. It was also decided to hold the increase in lab workload to 10 percent.

Over the life of the project some 20 to 30 individuals were involved in sample collection. Sample collectors operate out of 10 Water Survey and three Water Quality sub-offices scattered throughout the region. Sample collection and preservation should have followed the standard methods described in the field manuals always (Water Quality Branch, 1979a, Water Quality Branch, 1979b). However, within the standard methods there is considerable leeway. For instance, samples can be collected using a 2-L bottle on the standard sampling iron and then poured into the appropriate bottles for shipment or the bottles can be directly hand dipped (in shallow streams) or some combination of the two techniques. A second example is the preservation of samples using either ampoules or a reagent dispenser bottle. Among the other possible causes of poor precision that this report deals with, two variables in sample handling are included: filtration in the field versus in the lab and transit time to the laboratory.

All of the chemical analyses involved in this study were conducted at the Water Quality Branch Regional Laboratory in Calgary. Table 1 lists the parameters studied, along with their abbreviations and National Water Quality Data Bank (NAQUADAT) parameter code. Descriptions of the analytical methods used can be found by referring to the appropriate parameter code in the NAQUADAT dictionary reference, or to the Analytical Methods Manual (Water Quality Branch, 1979c). Most of the parameters under discussion were analysed by the same method over the period of interest. However, DIC, DOCL and TOC were done by two different methods over the course of the study. Also, there may have been minor changes made in analytical methods which were not considered significant enough to change the parameter code. Changes in the analytical method add to the variance of measurement over the period of study. The Calgary laboratory was able to provide analytical precision data for 12 of the 18 nutrient parameters studied. These data are listed in Table 2.

The computation of the coefficient of variation in percent is as follows:

$$CV = s / \bar{y} \times 100\%$$

where s = standard deviation of replicate samples ($n = 2$ or 3)
and $\bar{y}$ = arithmetic average of replicate samples.

When a concentration was reported as less than the detection limit, half of the limit was used in the computation of s and $\bar{y}$ since the author considered this to be the least biased estimate of the true concentration.

RESULTS

The interpretation of the results of this project rests on two major assumptions. The first is that a coefficient of variation computed on two observations is equivalent to one computed

TABLE 1. List of parameters studied

Parameter Name	Abbr.	Parameter Code
Total Organic Carbon	TOC	06001L, 06005L
Dissolved Organic Carbon - Field Filtered	DOCD	06104D
Dissolved Organic Carbon - Lab Filtered	DOCL	06101L, 06104L
Dissolved Inorganic Carbon - Lab Filtered	DICL	06151L, 06152L
Particulate Organic Carbon - Field Filtered	POCF	06902F
Particulate Organic Carbon - Lab Filtered	POCL	06902L
Nitrate Nitrite - Field Filtered	NOD	07110D
Nitrate Nitrite - Lab Filtered	NOL	07110L
Ammonia	NH3	07506L
Dissolved Nitrogen - Field Filtered	DND	07651D
Dissolved Nitrogen - Lab Filtered	DNL	07651L
Paticulate Nitrogen - Field Filtered	PNF	07902F
Paticulate Nitrogen - Lab Filtered	PNL	07902L
Dissolved Phosphorus - Field Filtered	DPD	15103D
Dissolved Phosphorus - Lab Filtered	DPL	15103L
Ortho-Phosphorus - Field Filtered	OPD	15256D
Ortho-Phosphorus - Lab Filtered	OPL	15256L
Total Phosphorus	TP	15406L

on three. This assumption is made in order to include as much of the data as possible. The second assumption has to do with the manner in which the data are treated after analysis. The Branch uses a rather sophisticated data screening procedure involving, since 1978, a computer, several people in the lab and the officers responsible for the water quality assessment programs. The computer treats quality control samples identically to all other samples. However, the humans in the process will tend to look at them as a set, thereby increasing the probability that anamolous data will be intercepted prior to reporting. This means that any estimate of total precision based on these data will be biased low. It is impossible to say what the magnitude of the bias might be.

Table 3 summarizes the results grouped by fiscal year. The median coefficient of variation in this table is the estimate of total precision. Generally speaking, the total precision of a parameter is fairly constant from year to year whereas the maximum coefficients of variation fluctuate considerably. There are some patterns in the results which may be significant. For instance, there are six parameters whose field filtered version (DOCD, POCF, NOD, DND, PNF and DPD, see Table 1 for expansion of abbreviations) can be compared to the lab filtered version (DOCL, POCL, NOL, DNL, PNL and DPL). The total precisions of the four dissolved

TABLE 2. Analytical precision of nutrient tests

No. of sets	No. of observations per set	Range of sets or mean of 1 set in mg/L	Precision in %
Dissolved Organic Carbon - Lab Filtered (DOCL)			
6	2	0.3 - 0.9	17.94
9	2	2.75 - 5.40	5.05
13	2	8.35 - 13.50	4.13
Dissolved Inorganic Carbon - Lab Filtered (DICL)			
4	2	27.0 - 33.5	1.74
Nitrate Nitrite - Field Filtered (NOD)			
4	2	0.24 - 0.38	2.62
Nitrate Nitrite - Lab Filtered (NOL)			
1	7	0.025 0.00	
5	2	0.04 - 0.20	4.17
1	7	0.200 0.00	
1	7	0.501 0.80	
Ammonia (NH3)			
5	2	0.17 - 0.60	9.01
Dissolved Nitrogen - Field Filtered (DND)			
4	2	0.07 - 0.15	0.00
4	2	0.24 - 0.36	1.29
10	2	0.78 - 1.10	4.23
Dissolved Nitrogen - Lab Filtered (DNL)			
1	10	0.050 0.00	
1	10	0.296 1.69	
1	10	0.755 1.32	
Dissolved Phosphorus - Field Filtered (DPD)			
4	2	0.053 - 0.062	0.60
4	2	0.40 - 0.42	0.00
Dissolved Phosphorus - Lab Filtered (DPL)			
4	2	0.008 - 0.025	0.00
5	2	0.11 - 0.20	0.00
Ortho-Phosphorus - Field Filtered (OPD)			
4	2	0.0145 - 0.034	1.92
Ortho-Phosphorus - Lab Filtered (OPL)			
4	2	0.019 - 0.094	0.00
Total Phosphorus (TP)			
1	7	0.008 12.5	
1	7	0.196 2.55	
4	2	0.16 - 0.29	0.00
1	7	0.400 1.50	

TABLE 3. Summary by Year

Fiscal Year	No. of Sets	Range of Sets or mean of 1 set in mg/L	Coefficient of Variation in percent		
			Minimum	Median	Maximum
Total Organic Carbon (TOC)					
1977	5	2.83 - 22.	0	9	100
1978	2	7.5 - 11.7	5	43	82
1980	10	2. - 26.7	0	3	43
1981	1	12.	0	0	0
1977 to 1981	18	2. - 26.7	0	7	100
Dissolved Organic Carbon - Field Filtered (DOCD)					
1980	19	2. - 17.	0	0	78
Dissolved Organic Carbon - Lab Filtered (DOCL)					
1978	36	0.5 - 26.3	0	1	66
1979	43	0.5 - 26.3	0	0	43
1980	16	2. - 26.7	0	4	50
1981	37	0.4 - 25.	0	1	15
1977 to 1981	132	0.4 - 26.7	0	0	66
Dissolved Inorganic Carbon - Lab Filtered (DICL)					
1978	36	6.33 - 70.	0	2	21
1979	43	0.5 - 84.	0	0	31
1981	2	30. - 42.7	0	1	1
1977 to 1981	81	0.5 - 84.	0	1	31
Particulate Organic Carbon - Field Filtered (POCF)					
1977	11	0.19 - 6.73	9	32	52
Particulate Organic Carbon - Lab Filtered (POCL)					
1977	86	0.075 - 3.8	0	14	90
1978	36	0.0533 - 9.89	3	10	70
1979	43	0.04 - 7.13	2	13	79
1980	30	0.15 - 13.3	0	5	48
1981	39	0.0733 - 8.97	0	7	80
1977 to 1981	234	0.04 - 13.3	0	10	90
Nitrate Nitrite - Field Filtered (NOD)					
1980	19	0.005 - 1.03	0	0	71
1981	30	0.005 - 1.47	0	0	43
1977 to 1981	49	0.005 - 1.47	0	0	71
Nitrate Nitrite - Lab Filtered (NOL)					
1977	5	0.005 - 1.3	0	0	77
1978	38	0.005 - 1.67	0	3	95
1979	43	0.005 - 0.513	0	6	152
1980	15	0.005 - 0.143	0	0	157
1981	9	0.005 - 0.07	0	0	144
1977 to 1981	110	0.005 - 1.67	0	3	157
Ammonia (NH3)					
1977	1	0.05	0	0	0
1978	4	0.05 - 0.367	0	8	42
1979	7	0.05 - 0.767	0	0	8
1980	2	0.0667 - 0.0667	43	43	43
1981	28	0.05 - 0.5	0	0	11
1977 to 1981	42	0.05 - 0.767	0	0	43

Table 3. (continued)

Fiscal Year	No. of sets	Range of Sets or mean of 1 set in mg/L	Coefficient of Variation in percent		
			Minimum	Median	Maximum
Dissolved Nitrogen - Field Filtered (DND)					
1980	18	0.12 - 1.67	0	2	12
1981	28	0.07 - 1.6	0	2	16
1977 to 1981	46	0.07 - 1.67	0	2	16
Dissolved Nitrogen - Lab Filtered (DNL)					
1978	36	0.0667 - 1.6	0	5	65
1979	43	0.07 - 1.1	0	4	36
1980	34	0.0933 - 1.5	0	3	110
1981	39	0.07 - 1.6	0	4	36
1977 to 1981	152	0.0667 - 1.6	0	4	110
Particulate Nitrogen - Field Filtered (PNF)					
1977	11	0.0383 - 2.22	5	53	132
Particulate Nitrogen - Lab Filtered (PNL)					
1977	83	0.005 - 4.93	0	17	166
1978	36	0.01 - 2.68	0	11	121
1979	43	0.005 - 0.637	0	22	134
1980	35	0.0067 - 2.66	0	11	120
1981	39	0.005 - 0.767	0	5	139
1977 to 1981	236	0.005 - 4.93	0	13	166
Dissolved Phosphorus - Field Filtered (DPD)					
1980	17	0.004 - 0.277	0	13	134
1981	30	0.0015 - 0.543	0	4	110
1977 to 1981	47	0.0015 - 0.543	0	6	134
Dissolved Phosphorus - Lab Filtered (DPL)					
1978	36	0.0013 - 0.32	0	5	50
1979	42	0.0015 - 0.227	0	3	62
1980	15	0.0015 - 0.05	0	17	44
1981	9	0.0015 - 0.0323	0	4	43
1977 to 1981	102	0.0013 - 0.32	0	4	62
Ortho-Phosphorus - Field Filtered (OPD)					
1981	10	0.0015 - 0.247	0	1	43
Ortho-Phosphorus - Lab Filtered (OPL)					
1977	1	0.0048	94	94	94
1978	7	0.0015 - 0.442	0	3	74
1979	4	0.0015 - 0.0363	0	2	78
1977 to 1981	12	0.0015 - 0.442	0	4	94
Total Phosphorus (TP)					
1977	242	0.0015 - 3.7	0	3	131
1978	71	0.0015 - 0.84	0	3	54
1979	43	0.0015 - 0.253	0	5	85
1980	31	0.0015 - 0.6	0	5	59
1981	38	0.0015 - 0.633	0	6	127
1977 to 1981	425	0.0015 - 3.7	0	3	131

parameters filtered in the field are at least as good as the corresponding lab filtered total precisions, while the two particulate parameters show poorer total precisions for the field filtered version. The maximum coefficients of variation for field filtered parameters are lower than their lab filtered counterparts with the exception of DOC and DP. It also appears tha POCL has shown some improvement in total precision during the last two years.

DISCUSSION

The total precision of each parameter is estimated by the median of the coefficients of variation computed on all sets for that parameter. The total precision can be compared numerically to the analytical precision.

Table 4 summarizes the comparison of total to analytical precisions.

TABLE 4. Comparison of Total and Analytical Precision

Parameter	Analytical Precision in %	Total Precision in %	Comparison
DOCL	4 - 18	0	BETTER
DICL	2	1	BETTER
NOD	3	0	BETTER
NOL	0 - 4	3	EQUAL
NH3	9	0	BETTER
DND	0 - 4	2	EQUAL
DNL	0 - 2	4	POORER
DPD	0 - 1	6	POORER
DPL	0	4	POORER
OPD	2	1	BETTER
OPL	0	4	POORER
TP	0 - 12	3	EQUAL

There are only four parameters, DNL, DPD, DPL and OPL, which show a total precision which is poorer (coefficient of variation greater) than the corresponding analytical precision.

However, this comparison is insufficient in terms of identifying problem parameters. The median coefficient of variation is only part of the story. By including maximum coefficient with the median coefficients, a two factor classification system can be set up. Fig. 1 depicts the system used. The boundaries were set somewhat arbitrarily and, therefore, the classification should be viewed as being indicative rather than definitive.

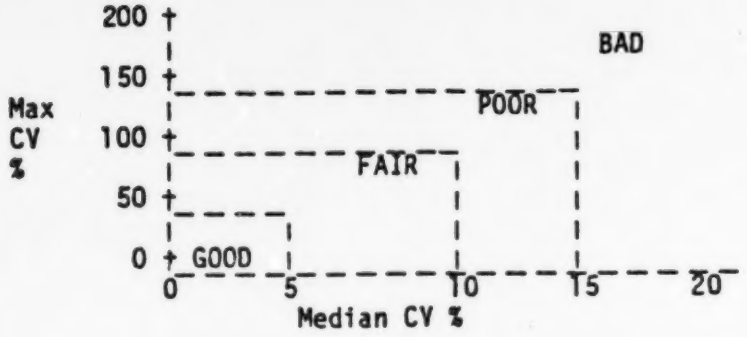

Fig. 1: Classification of total precisions.

Table 5 classifies each parameter according to the system depicted in Fig. 1. The parameters are evenly distributed among the four classes.

TABLE 5. Classification of Results

Parameter	Median CV in %	Maximum CV in %	Class
TOC	7	100	FAIR
DOCD	0	78	FAIR
DOCL	0	66	FAIR
DICL	1	31	GOOD
POCF	32	52	BAD
POCL	10	90	FAIR
NOD	0	71	FAIR
NOL	3	157	BAD
NH3	0	43	GOOD
DND	2	16	GOOD
DNL	4	110	POOR
PNF	53	132	BAD
PNL	13	166	BAD
DPD	6	134	POOR
DPL	4	62	FAIR
OPD	1	43	GOOD
OPL	4	94	FAIR
TP	3	131	POOR

Total precision is a statistic and therefore has a distribution. This distribution could have a non-random component (Guilbault, 1981). As a first pass examination of this possibility, correlation coefficients for the coefficients of variation against selected independent variables were computed. Wilson (1976) and others have stated that the precision of measurement is dependent on the concentration, so, the mean concentration of the set was selected. River discharge was selected as an indicator of some of the in-stream processes which might contribute to the variance of the set. The last independent variable to be considered is transit time from the point of sampling to the laboratory. Inclusion of this variable was suggested by the work of V. T. Chacko (personal communication) on sample holding time for nutrient parameters.

Correlation coefficients were computed on sets grouped by fiscal year and by site. This produced 583 correlation coefficients of which 145 or 25% had a magnitude greater than 0.707 (determination greater than 50%). The grouping by site was indicated by previous work on particulate nutrient parameters (Guilbault, 1981) which showed that the relationship between the standard deviation and mean of a set for particulate nutrient parameters varied from site to site.

Although 25% of the coefficients of correlation are greater than 0.707, only about 2% of the groups consisting of 10 or more sets show coefficients greater than 0.707. There appears to be little correlation of precision to either mean concentration, river discharge or transit time to the laboratory. This is not to say, however, that there is no relationship between the variables, but simply that the relationship, if it exists, is not linear. Examination of the 20 sets with the worst CV's indicates that, although most of the anomalies are inexplicable, what evidence there is points to a wide variety of possible causes for poor precision. This relates back to the lack of correlation since large, random errors can mask a correlation even if the errors are of low frequency.

Guilbault (1981) also suggests that a more detailed examination of sets with large coefficients of variation can shed added light on the possible causes of poor precision. The 20 sets with the largest CV's were investigated in detail. The sampler's and analyst's notes and computations were reviewed for any evidence of a problem in handling the set. The corresponding non-filterable residue (suspended sediment) data, where available, were also examined.

Table 6 lists these sets and the results of the examination. Of the 20 sets, 14 were collected during fiscal year 1977, which pre-dates the introduction of computer assisted data verification in the laboratory. Fourteen are for the parameter Particulate Nitrogen - Lab Filtered (PNL) and 14 were collected from sites within the Province of Saskatchewan. The latter observation may be an artifact of the distribution of sites at which PNL is

TABLE 6: Twenty cases with the poorest precision

CV	Parameter	Station	Date	Replicates			Remarks
166	PNL	00SA06EA0003	20/12/77	0.005	0.05	1.8	
162	PNL	00SA05JM0014	21/12/77	0.005	0.1	2.3	Lab noted 2.3 is "no good"
159	PNL	00SA05FE0001	13/07/77	0.32	0.48	14.	
159	PNL	00SA06EA0003	24/08/77	1.9	0.06	0.95	
157	NOL	00SA07MA0001	04/06/80	0.005	0.02	0.38	NFR < 1. 1. 1.
152	NOL	00AL05CK0001	17/07/79	0.11	0.005	0.005	NFR 424 422 436
148	PNL	00SA05FE0001	16/08/77	1.5	0.08	0.08	
147	PNL	00SA05MD0002	23/11/77	0.09	0.005	0.005	NFR 4. 6. 4.
144	PNL	00SA05EF0001	14/12/77	0.08	0.005	0.005	
144	NOL	00NW06LC0001	14/07/81	0.005	0.005	0.08	NFR < 1. < 1. 1.
141	PNL	00AL05AK0001	13/12/77	0.005	0.005	0.07	
141	PNL	00SA05JM0014	24/11/77	0.07	0.005	0.005	
140	PNL	00SA05JM0014	25/08/77	0.54	7.4	0.54	NFR 76. 78. 73.
139	PNL	00AL07AA0023	21/04/81	0.005	0.1	0.01	NFR 11. 11. 13.
136	PNL	00SA05FE0001	18/10/77	0.005	0.06	0.005	
135	PNL	00SA05KH0002	22/11/77	0.005	NV	0.23	Instrument failed to integrate second replicate
134	PNL	00AL07GJ0001	11/06/79	NV	0.18	0.005	NFR 23. 203 239
134	DPD	00AL05CK0001	10/06/80	0.009	0.1	0.009	Typo - 0.1 should be 0.01
132	PNF	00SA05KH0002	20/09/77	0.13	0.005	0.02	
131	TP	00SA07LA0001	14/02/78	0.13	0.015	0.01	NFR < 1. < 1. < 1.

The results of the Field Quality Control Project, to date, point to a complex error distribution associated with the measurement of water quality parameters in the Western and Northern Region. The size of the tail of that distribution can impact detrimentally on certain kinds of water quality data interpretation. The large variances which are occasionally observed in time series of less than one hour in length could mask small but significant trends in longer, less frequently sampled series.

Data interpreters should be aware of the distribution of uncertainties in the measurement of water quality parameters in order to avoid potential problems. The data collector on the other hand must understand the distribution in order to control it in a cost effective manner. To control the uncertainities in the measurements economically, quality control should concentrate on the most error-prone steps in the sampling and analysis procedures. In order to do this, all steps and the impact of errors at each step on the measurement must be identified.

CONCLUSIONS

Only DICL, NH3, DND and OPD, of the 18 parameters studied show "good" precision by the criteria herein defined. The evaluation of precisions point to some seven problem parameters: POCF, NOL, DNL, PNF, PNL, DPD and TP.

The total precision cannot be tied to mean concentration, river discharge or time in transit between the point of sampling and the laboratory. The precision does not vary linearly with any of these.

Poor precision can be attributed to random errors, which can occur anywhere along the measurement process, from sample collection, through laboratory analysis, to data reporting.

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POOR

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